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Single-Crystal Germanium Films by Micro-Zone Melting

J. Maserjian

This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7-100) sponsored by the National Aeronautics and Space Administration.

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SINGLE-CRYSTAL GERMANIUM FILMS BY MICRO-ZONE MELTING*†

J. MASERJIAN

Jet Propulsion Laboratory, California Institute of Technology, California

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Abstract—A technique has been developed for growing single-crystal germanium films *in situ* on a dielectric substrate. An electron beam is used to melt a small zone of a polycrystalline germanium film. Single-crystal growth is induced by electrically scanning the beam in a preferred manner over a selected region of the film. An additional heat source maintains the surrounding film at elevated temperatures in order to avoid excessive temperature differentials. The scanning pattern employed permits a randomly nucleated crystallite to seed the surrounding growth. In this manner, a single-crystal the order of a millimeter across can be grown in a chosen location. Larger crystals should be possible with larger beam deflections.

This work has been largely confined to film thicknesses of 3–10 μ and to substrates of sapphire. Sapphire was used because its coefficient of thermal expansion closely matches that of germanium and because of other desirable properties. All films were deposited by vacuum evaporation.

The technique is logically extendable to other materials that can be grown in vacuum. It is anticipated that the technique will find applications in microelectronics and in the fabrication of special device structures.

AUTHOR

Résumé—On a tracé une technique pour développer des pellicules de germanium à cristal unique sur une couche inférieure de diélectrique *in situ*. Un faisceau d'électrons est employé pour fondre une petite zone de la pellicule de germanium polycristallin. Le développement de cristal unique est induit en balayant électriquement le faisceau d'une manière préférée sur une région choisie de la pellicule. Une source de chaleur supplémentaire maintient la pellicule environnante à des températures élevées pour éviter des différences de température excessives. Le modèle de balayage employé permet à un cristal nucléé au hasard de semer le développement environnant. De cette façon, un cristal unique de l'ordre d'un millimètre de largeur peut être développé dans un endroit choisi. De plus grands cristaux devraient être possible avec de plus grandes déflexions de faisceau.

Ce travail a été surtout limité à des épaisseurs de pellicule de 3–10 μ et aux couches inférieures de saphir. Le saphir a été employé grâce à son coefficient d'expansion thermique qui s'adapte à celui du germanium ainsi qu'à d'autres propriétés désirables. Toutes les pellicules ont été déposées par l'évaporation à vide.

Cette technique est logiquement étendue à d'autres matériaux qui peuvent être développés dans le vide. On s'attend à ce que cette technique trouve des applications dans la micro-électronique et dans la fabrication des structures de dispositifs spéciaux.

Zusammenfassung—Ein Verfahren zur Erzeugung von Germanium Einkristall-Filmen *in situ* auf einem dielektrischen Substrat wurde entwickelt. Ein Elektronenstrahl dient zum Schmelzen einer kleinen Zone eines polykristallinen Germaniumfilms. Das Wachstum des Einkristalls wird durch elektrisches Abtasten des Strahles eingeleitet und zwar mit Bevorzugung einer ausgewählten Zone des Films. Eine zusätzliche Wärmequelle erhält den umgebenden Film bei erhöhter Temperatur zur Vermeidung starker Temperaturunterschiede. Die Abtastung wird so ausgeführt, dass ein zufalls-mässig gebildeter Kristallitkern das Kristallwachstum in der Umgebung einleitet. Auf diese Weise kann ein Einkristall mit einer Breite der Grössenordnung 1 mm an einer beliebig gewählten Stelle gezogen werden. Bei grösserer Ablenkung des Strahls könnte man wohl grössere Kristalle herstellen.

* This paper presents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100 sponsored by the National Aeronautics and Space Administration.

† Much of this work was presented at Solid State Device Research Conference, Durham, New Hampshire, July, 1962.

Diese Arbeit beschränkte sich auf Filmdicken von 3–10 μ mit einem Saphir-Substrat. Der Saphir wurde benutzt, weil sein Wärmeausdehnungskoeffizient dem von Germanium fast gleich ist und er auch sonst günstige Eigenschaften besitzt. Alle Filme wurden im Vakuum aufgedampft.

Das Verfahren lässt sich auf andere Materialien ausdehnen, die man im Vakuum ziehen kann. Es ist anzunehmen, dass es in der Mikroelektronik und bei der Herstellung spezieller Geräteteile Anwendung finden wird.

I. INTRODUCTION

THE method of growing single-crystal semiconductor films by epitaxy on single-crystal substrates of the same or similar materials is now well known.⁽¹⁾ This paper describes a method of growing single-crystal germanium films on an inert substrate without epitaxy. The work was stimulated by the need in microelectronics for a method of producing semiconductor active devices *in situ* on an insulating substrate.⁽²⁾ The method may also be useful for certain devices requiring thin structures with relatively high resistivity regions. The material presented is confined to the experimental results and the techniques used. The effects of the various experimental parameters are discussed.

The method employs an electron beam that melts a small region or zone of the film and is scanned across an area of the film in a particular manner. The process of melting and recrystallization is similar on a microscopic scale to the commonly used zone-melting process.⁽³⁾ Seeding is accomplished by crystal grains that survive the imposed growth pattern and, in some ways is related to the method of TAMMANN⁽⁴⁾ (also commonly accredited to BRIDGMAN).⁽⁵⁾

It has been brought to our attention that LEITZ has described a zone-melting process for growing single-crystal films of luminescent materials on insulating substrates.⁽⁶⁾ This process uses TAMMANN's method of seeding by depositing the film in a pattern tapered to a fine line at one end, and subsequently zone-melting from this tapered end. The molten zone is produced by a heated platinum wire that extends over the width of the film. Our experience has been that such an extended molten zone is unstable and would collapse under the influence of surface tension (at least for the materials examined in our experiments).

II. EXPERIMENTAL TECHNIQUE

Fig. 1 schematically represents the situation in which an electron beam is used to form the

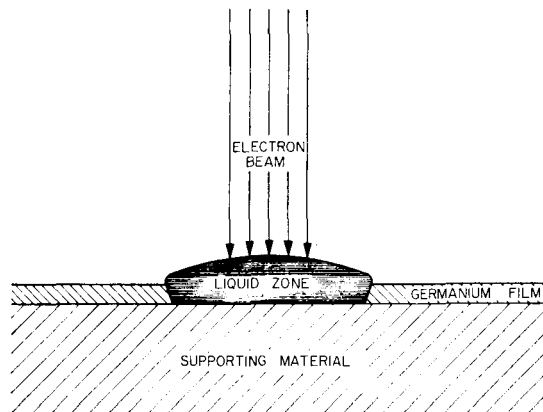


FIG. 1. Schematic representation of electron-beam zone-melting of germanium film.

molten zone in the film. The mounding of the zone results from surface tension and is important in limiting the size of the zone and the manner of scanning. The system is also heated uniformly to about 850°C by a radiant heater to minimize the thermal gradient between the molten zone and the surrounding material. By electrically deflecting the electron beam, the molten zone is made to scan the film in a preferred manner. As continuous melting and recrystallization takes place, the adjacent film acts to seed the growth occurring along the trail of the moving molten zone. Very small crystallites grow initially, but, by overlapping the path of the moving zone, relatively few large crystallites of preferred orientation survive. This process is developed further by means of a more elaborate scanning pattern, so that a single-crystal is grown over a selected area.

It is advantageous to have the molten zone as large as possible for reasons discussed in Section V. If the zone is made too large, surface tension can cause it to collapse into molten beads at the periphery. Also for this reason, the zone must always be surrounded by germanium film, as it will collapse from an unbounded edge. In practice the zone diameter was made as large as fifty times

the film thickness. The horizontal scale in Fig. 1 has been considerably compressed. In general, the zone diameter can be controlled by adjusting the beam current and the heater temperature. Normally the heater was controlled to a constant temperature and the beam current adjusted (typically $10\mu\text{A}$ at 50 kV). It is desirable to distribute the beam energy to avoid excessive temperatures and evaporation of germanium at the center of the zone. This was accomplished by deflecting the beam at 4 kc/s into a Lissajous circle slightly smaller than the zone.

Most experiments have been performed on germanium films evaporated on mechanically polished sapphire substrates. Sapphire was used primarily because its thermal expansion coefficient closely matches that of germanium, it is relatively pure, and in general is inert to the process. Its crystalline structure is incidental in this case and (as will be discussed later) does not enter into the growth process. Germanium films of thickness ranging from 3 to 10μ were found most convenient for the experimental conditions employed. A Zeiss interference microscope was used for measuring thickness. Best results were obtained when the germanium was evaporated rapidly ($>10^{-5}\text{ cm/sec}$) on to a heated substrate (approximately 800°C). Lower rates and temperatures resulted in pinholes and blisters in the films that would often cause the liquid zone to collapse during the electron-beam melting process. The evaporation source was either a germanium-wetted tungsten filament or an electron-bombarded tantalum crucible containing a measured quantity of germanium. The germanium source material was taken from n -type single-crystals of a few ohm-centimeters resistivity. Vacuums were maintained at less than 1×10^{-6} torr during evaporation.

III. THE ELECTRON-BEAM APPARATUS

An RCA-EMU electron microscope already available was adapted to this work. The sample is located within the diffraction chamber of the microscope, and the projector pole-piece of the microscope is replaced with the system shown in Fig. 2. The sample is surrounded by a heater with a water-cooled jacket, which is inserted through one of the windows of the diffraction chamber. The sample is attached to a micrometer movement that can be motor driven and is inserted through the

opposite window. The collimated electron beam is focused on the specimen surface with a specially designed pole-piece that uses the field winding of the microscope projector lens. Two magnetic coils

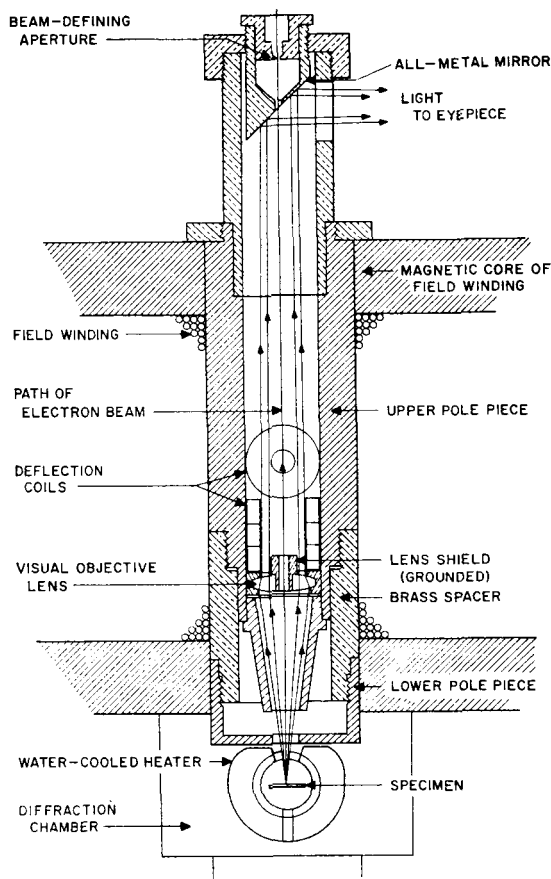


Fig. 2. Arrangement of electron-beam zone-melting apparatus inside RCA-EMU electron microscope.

located inside the pole-piece provide a means of deflecting the beam in any manner. The beam current can be measured by retracting the specimen and allowing the beam to pass through a hole in the bottom of the heater chamber to a Faraday cage below. Melting may be observed through an optical system coaxial with the electron beam as illustrated. Sufficient light is provided by the heater filament.

Restricted space in the electron microscope was a serious limitation in the design of the apparatus.

The pole-piece design was a compromise based on LIEBMANN's data⁽⁷⁾ and the physical constraints of the microscope. The necessity for deflecting the beam above the electron lens restricted the scanning distance to about 1 mm.

IV. EXPERIMENTAL RESULTS

Fig. 3 is a photomicrograph of a germanium film recrystallized by simply overlapping the path of the molten zone along one direction. The etching and dark-field illumination clearly delineate the different crystal grains. The black areas represent crystal grains of (111) orientation parallel to the surface. This sample was prepared by scanning the molten zone sinusoidally at 1 c/s in one direction while traversing transverse to the scan with the mechanical drive at $3 \mu/\text{sec}$. It is clear that only a few crystallites of preferred orientation survive this process of growth. The crystallites are seen to be small near the limits of the scanned region. At the extreme edge of the region the minute grains of the evaporated film act as seeds, and correspondingly fine crystallites start to grow. This is seen better in the electron-micrograph of Fig. 4 taken at the edge of a melted region. No etch was used on the specimen and the grain boundaries are less distinct. The original evaporated film is at the upper right where the grains are seen to average a fraction of a micron across. Close inspection reveals that the grains at the boundary of the melted region have seeded the adjacent growth. As growth continued away from the boundary, the crystallites became larger. Ultimately these crystallites would have met those growing from the other sides of the molten zone. However, by overlapping the path of the zone, growth can be effectively continued along one direction, and, as seen in Fig. 3, only a few large crystallites survive. The tilt in the general direction of the elongated crystallites occurred merely because the scan was tilted.

Micrographs such as that shown in Fig. 3 reveal no apparent seeding by the underlying substrate. In each case where nucleation of new crystallites occurs within the region, it can be traced to a serious defect such as at a grain boundary. Irregularities in the substrate surface such as scratches may, however, have an influence on the location and direction of some of the grain boundaries. The sapphire substrate was oriented

with the surface normal 60° to the c -axis of the hexagonal structure and bears little relation to the germanium. Also the extreme surface damage caused by the mechanical polishing makes any argument favoring an epitaxial mechanism highly improbable.

The process described above may be extended to the growth of single crystals over a selected area by periodically rotating the direction of growth. If, after scanning an area of the film along one direction, one rotates the directions of scan and traverse 90° and continues out from the interior of the area, much larger crystallites will grow from the wider seeds. The pattern applied to the moving zone is illustrated in Fig. 5, where, for clarity, only one-fourth the number of scans are shown.

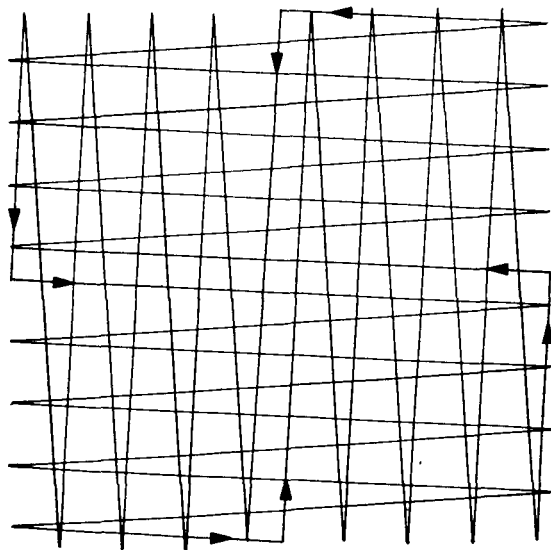


FIG. 5. Rotating scan pattern.

A complete 360° cycle required 1 min, and the process usually was allowed to complete at least three cycles. It is important that the molten zone follow a continuous path in the pattern so that the germanium is not redistributed in some non-uniform manner over the film. Redistribution would result because the molten zone is thicker than the surrounding film. For this reason, it is also necessary to terminate the process with the molten zone at the edge of the area. Other patterns such as spirals have been tried, but only the above pattern has been successful.

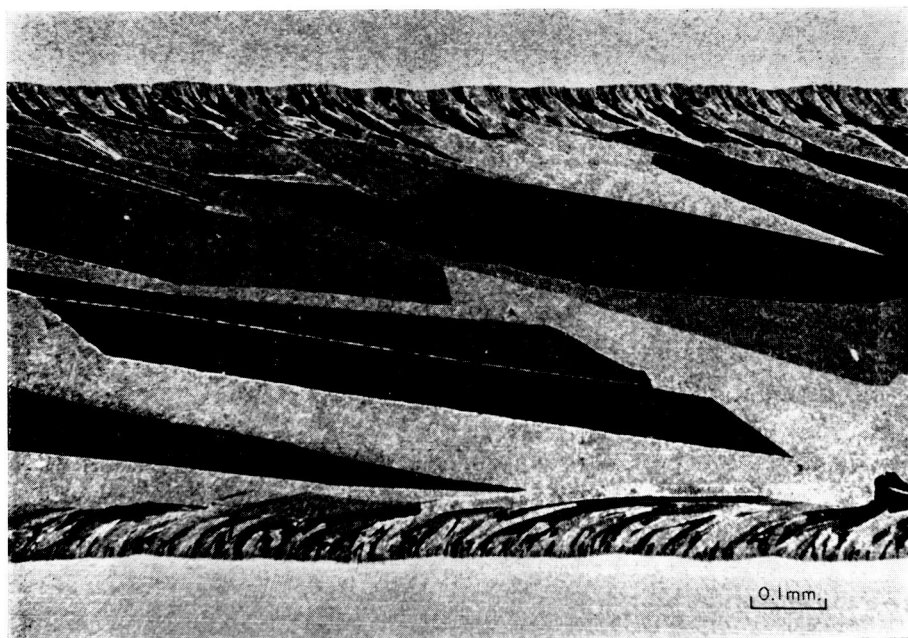


FIG. 3. Zone-melted germanium film (originally 4.6μ thick). Scanned with 0.1-mm dia. zone sinusoidally at 1 c/s and traversed at 3μ /sec from left to right. Sample given 15-sec WAg etch⁽⁸⁾ and shown under dark-field illumination.

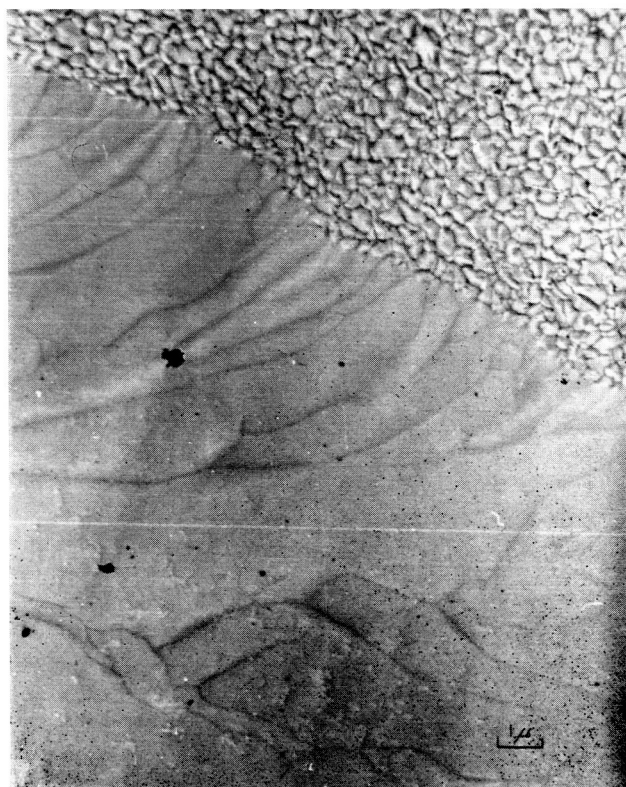


FIG. 4. Electron-micrograph showing boundary between zone-melted germanium film and original evaporated film.

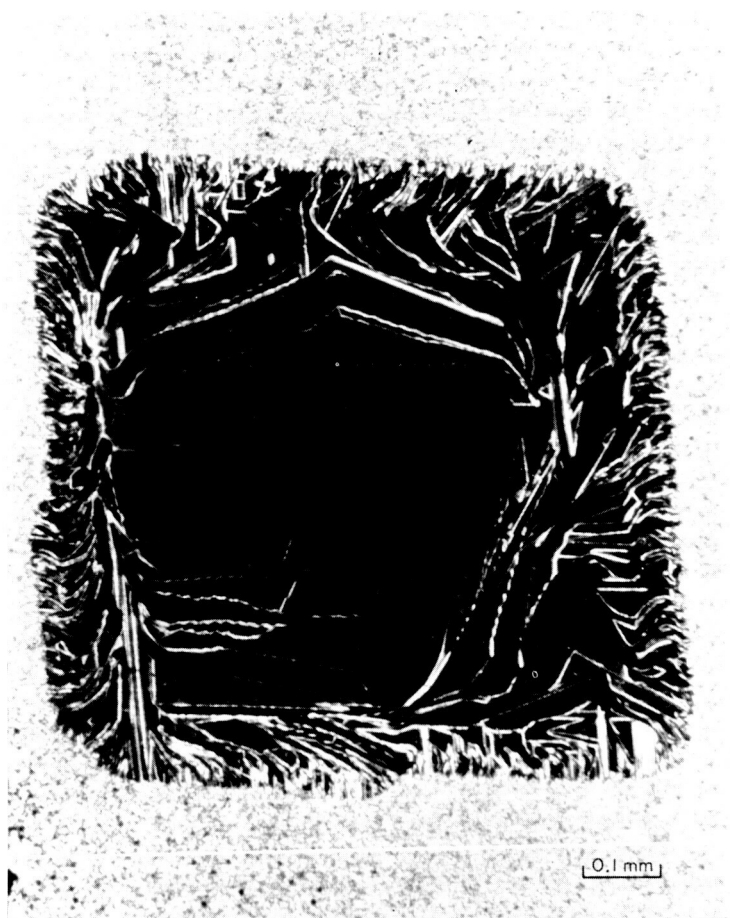
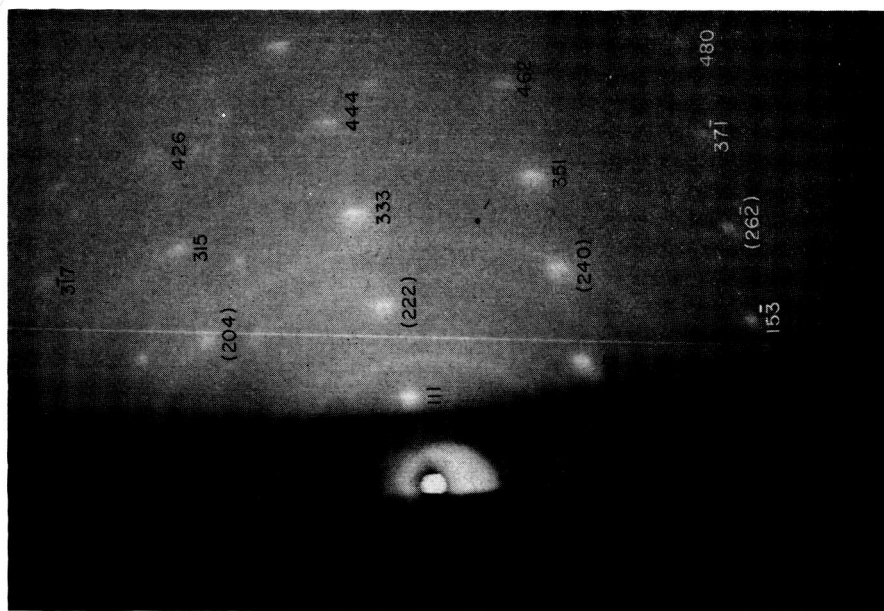
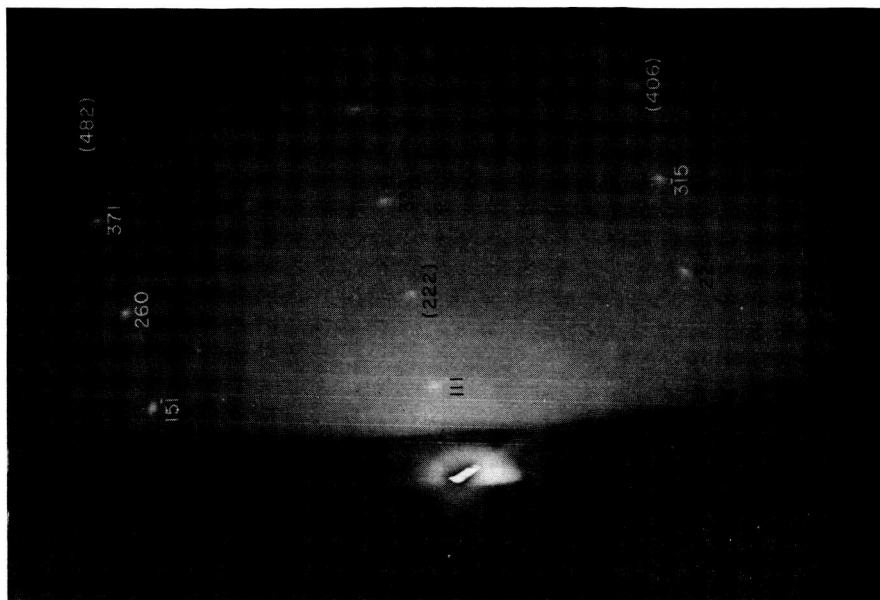


FIG. 6. Zone-melted germanium film obtained with rotating scan and 0.15 mm diameter zone (film originally $4.5\ \mu$ thick). Sample given 15-sec WAg etch⁽⁸⁾ and illuminated under dark-field.



(a)



(b)

FIG. 7. Electron diffraction patterns of sample shown in Fig. 5 taken at grazing incidence. (a) Reflections from (111) planes along $[211]$ direction. (b) Reflections from (111) planes along $[312]$ direction.



FIG. 8. Central area of sample of Fig. 6 under oblique illumination.

Fig. 6 is a photomicrograph of a germanium film recrystallized in the manner just described. The zone-melted area is revealed by the etch and dark-field illumination to have predominantly (111) orientation parallel to the surface. A single-crystal appears to extend over the central portion of this area. This observation was supported by both X-ray and electron diffraction results. Because of the thinness of the germanium films, back-reflection Laue X-ray patterns of the germanium were confused by a strong background pattern due to the sapphire. This was further complicated by an inability to confine the X-ray beam exclusively to the central portion of the area. Points that could be definitely attributed to the germanium were often accompanied by weaker points oriented within a few degrees of them. These are believed due to those crystallites at the outer parts of the area, many of which are only slightly misoriented along the [111] axis with respect to the central area.

Electron-diffraction patterns were more interpretable, and examples are seen in Fig. 7. The electron beam could not be confined exclusively to the central area, so that points attributed to the surrounding area are present. Additional points appearing symmetrically in the pattern (indexed with parentheses) commonly occur in electron diffractions at grazing incidence and probably arise from multiple diffractions. Debye rings from the adjacent untreated film and possibly some surface contamination are also visible. The results indicated that the two perpendicular scanned directions of the molten zone correspond to the $[\bar{2}11]$ and $[01\bar{1}]$ directions respectively of the central crystal. These would be the vertical and horizontal directions of Fig. 6. A good pattern for the $[01\bar{1}]$ direction was not obtained because several zone-melted regions were located in alignment along this direction, and additional points arising from the outer crystallites of each region confused the pattern.

Fig. 8 is a photomicrograph of the central portion of the same area shown in Fig. 6. The oblique illumination reveals the surface texture of the film. Except for the fine texture, which is not understood, the crystal surface is reasonably smooth. Lineage is evidenced by the lines emerging from the central crystal and continuing to the left. This is believed to arise as different arms growing

out from the central crystal fail to match precisely where they join at their boundaries.⁽⁹⁾ Shadows of shallow ridges along the vertical and horizontal directions may be detected, and are directly related to the path of the scanning molten zone. One would expect that the spacing of these paths as well as the scanning rates would have an important effect on the crystal growth. In Section V it is shown how they are related to the growth rate. Variations of the simpler scanning process described for Fig. 3 have been tried. These experiments showed that the slowest growth rates and closest spacing of scans give the best results. Therefore, different scanning and traverse frequencies may improve the crystal structure. Of course, the time required for the process must ultimately set a practical limit.

The heater temperature is also important. If the surrounding system is maintained at temperatures much less than the melting point of germanium, excessive stresses are created in the vicinity of the molten zone that can cause cracking of the sapphire or germanium film, or at least serious dislocations in the crystallized germanium. In the other extreme where the system is maintained very close to the melting point of germanium, the boundary of the molten zone is poorly defined and very weak thermal gradients exist. Under this condition a large part of the molten zone does not extend to the underlying sapphire but rides over the film. A different mode of growth occurs in the case that typically does not give (111) orientations. Phenomena, such as floating dendrites that become attached to the growing interface, are believed to have been observed during the process. These films generally grow very non-uniform in thickness. Difficulty is also experienced with the molten zone collapsing and consequently destroying the area. A compromise between these extremes of temperatures that gives satisfactory experimental results is at approximately 850°C.

Further information was obtained from Hall-effect measurements. It was necessary to form an appropriate pattern of the film that permitted measurement of only the area of interest. This was accomplished as follows: An aluminum film was evaporated over the germanium film to be measured. A photoresist process was applied over the aluminum to produce the desired pattern, see Fig. 9. The combination of aluminum and photo-

resist permitted removal of the surrounding film with a standard etch. The aluminum was then removed with HCl from the germanium pattern except at the contact areas. Attempts to use the photoresist process without the aluminum were unsuccessful.

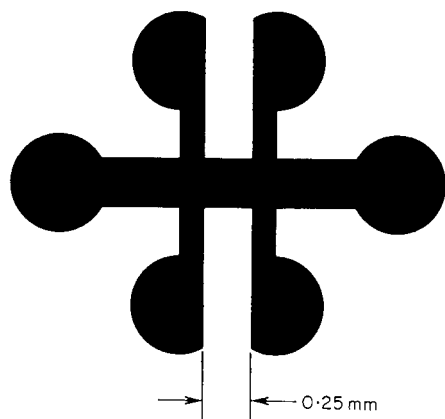


FIG. 9. Pattern used in photoresist process for Hall-effect measurements.

The measurements provided values of resistivity, carrier type, mobility, and carrier concentration. Table 1 compares the values measured

and low effective impurity concentration. This may be related to the fact that the crystal grains are relatively large with the evaporation method used, as seen in the electron-micrograph of Fig. 4. The zone-melted film has a mobility that compares favorably with the published values for highly perfect germanium single-crystals. There is no detectable lowering of mobility due to crystal lattice imperfections in this case. The larger experimental uncertainty associated with the zone-melted film arose because of the greater uncertainty in the film thickness after treatment. The p -type conductivity, determined by the Hall measurements, was also checked by detecting the thermoelectric effect with a hot probe. The change to p -type for lightly doped n -type sources is commonly observed for evaporated films and is believed to arise from acceptor centers associated with lattice defects. In the case of the zone-melted films, the vacuum distillation of the more volatile donors during the process would tend to leave an excess of acceptors arising from either impurities or lattice defects.

V. DISCUSSION

The final structure of the zone-melted film has been seen to depend on the crystal growth that proceeds in a net direction perpendicular to the scan. One may analyze this process further with the

Table 1. Hall-effect data

Material	Resistivity Ω -cm	Type	Hall mobility $\text{cm}^2/\text{V-sec}$	Carrier concentration cm^{-3}
Untreated evaporated germanium film	0.30	P	700 ± 50	3×10^{16}
Micro-zone-melted germanium film	0.67	P	1900 ± 500	5×10^{15}
High perfection germanium (Ref. 10)	0.30	P	1520	1.4×10^{16}
	0.67	P	1710	5.5×10^{15}

for an untreated evaporated film and a zone-melted film similar to that of Fig. 6 with published data for high-perfection single-crystal ingots at the corresponding resistivities.⁽¹⁰⁾ The untreated evaporated film shows a surprisingly high mobility

help of Fig. 10. This figure represents the molten zone of radius R moving with velocity u to the right and overlapping the previous scan with a spacing s . The net rate of growth at a point P on the trailing edge of the zone and in a direction y ,

perpendicular to u , is given by v , which can be expressed as follows:

$$\begin{aligned} v &= \frac{dy}{dx} u \\ &= \sqrt{\left(\frac{2Ry - y^2}{R - y}\right)} u \\ &\approx \sqrt{\left(\frac{2y}{R}\right)} \left(1 + \frac{3y}{4R}\right) u, \quad \text{for } y \ll R \end{aligned}$$

The maximum velocity that enters in the growth process occurs at $y = s$ and is

$$v_m \approx \sqrt{\left(\frac{2s}{R}\right)} \left(1 + \frac{3s}{4R}\right) u \quad (1)$$

In equation (1), the traverse velocity v_0 has been neglected, since it is much smaller than v_m . On the

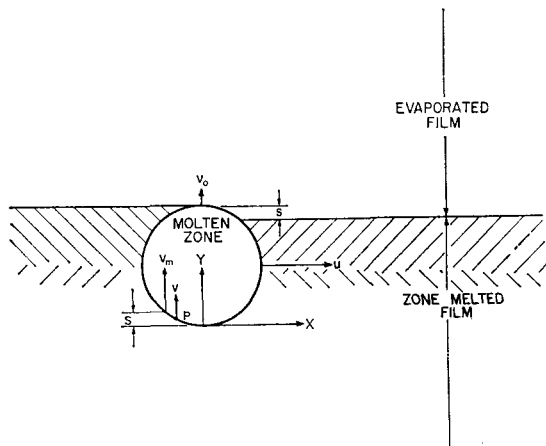


FIG. 10. Representation of moving molten zone.

basis that the growth rate and consequently v_m should be small, it is clear that u and s should be minimized and R maximized. However, as previously mentioned, considerations of process time and surface tension set practical limits. In the process applied to the sample of Figs 6 and 8, v_m was 1.5 mm/sec. This is believed to be near an upper limit for establishing single-crystal growth. In terms of parameters that apply to the rotating scanning pattern of Fig. 5, v_m becomes:*

$$v_m \approx 2L \sqrt{\left(\frac{2Lf_s f_0}{R}\right)} \left(1 + \frac{3Lf_0}{4Rf_s}\right) \quad (2)$$

where f_s and f_0 are the scanning and traverse frequencies, respectively, and L is the length of the pattern.

Another consideration concerns the uniform thickness of the zone-melted area and involves the scanning frequencies. The smallest overlap spacing has been found to give the most uniform thickness. It is therefore desirable to have a high ratio of f_s to f_0 . Equation (2) suggests increasing f_s and decreasing f_0 in the same proportion so that v_m is constant. An upper limit on f_s is determined, however, by the thermal relaxation time of the system. If the heat transfer cannot keep pace with the moving zone, the energy becomes smeared out over its trail. If the zone is near its critical size as determined by surface tension, it may collapse as it becomes too elongated. Alternatively, the energy density becomes insufficient for melting to extend to the underlying sapphire, and the molten zone rides over the germanium film. This has been detected by examining the reverse side of the treated film through the transparent sapphire substrate.

An estimate is derived for the maximum velocity as follows: The time required for the zone to move its radius R is set equal to the thermal diffusion time for the same distance; i.e.

$$t = R/u_m = R^2/\kappa$$

or

$$u_m = \kappa/R \quad (3)$$

where u_m is the maximum velocity permitted for the moving zone and κ is the thermal diffusivity of the medium. One may neglect the film and consider only the substrate. The value of κ for sapphire at 850°C is 0.014 cm²/sec, and, for $R = 10^{-2}$ cm, one calculates $u_m = 14$ cm/sec. For $L = 0.1$ cm, the maximum scan frequency is 7 c/s. This is consistent with experiment.

Nothing has been said in the above discussion about the detailed mechanism of the crystal growth. Such a discussion would be highly speculative and will not be attempted. The features that have been described depend only on a general mechanism involving seeding and growth from the

* The expression is derived using the mean value of s , which in general varies with position depending on the shape of the oscillation.

adjacent film and are independent of the detailed manner in which the crystal interface grows. This process is distinct from an epitaxial one, in which the growth occurs from the substrate.

The method has been demonstrated only for germanium on sapphire. However, it is reasonable to expect it to apply to other materials. An alternate substrate may be a pure form of alumina with a surface suitably glazed to avoid the surface-pitting characteristic of polished alumina. Attempts to apply the process to silicon were frustrated by the failure to find a suitable substrate; however, the search was not exhaustive.

Other work has recently been reported on the use of the electron beam for crystallizing germanium films. WEINREICH and DERMIT⁽¹¹⁾ have reported producing large crystallites on tungsten by electron-beam melting of the film. Because of the reactive nature of the germanium tungsten interface, an epitaxial process may have been involved in this case. GILBERT *et al.*⁽¹²⁾ have reported electron-beam scanning of germanium films that were evaporated on glass substrates. They claim that crystallization was accomplished slightly below the melting point of the germanium.

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